CHEMICAL REACTIVITY TEST FOR THERMAL STABILITY

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ABSTRACT

Lawrence Livermore National Laboratory (LLNL) has developed a thermal stability test procedure that is currently being evaluated by the Department of Defense (DOD) Explosives Safety Board as an equivalent alternate test to the DOD Technical Bulletin 700-2 “Thermal Stability Test at 75º C”.[1] This procedure will also be submitted for evaluation for acceptance under the similar test specified in the *United Nations Recommendations on the Transport of Dangerous Goods, Tests and Criteria Manual*.[2] The LLNL Chemical Reactivity Test (CRT) is significantly more severe than the existing "Thermal Stability Test at 750 C" and is also quantitative in nature. It has been approved by the Department of Energy (DOE) Explosives Safety Committee[3] as an equivalent alternate thermal stability test and has been in use by LLNL for over 30 years.[4,5] It is currently used by other DOE and DOD organizations as the standard small-scale safety test for determining thermal stability and material compatibility.

The LLNL CRT is run on a 0.250 gm sample for 22 hours at 120º C rather than the 50 gm sample for 48 hours at 750 C as required for the Thermal Stability Test. Thus the CRT is a much more severe test since it is run at 120º C rather than 750 C. Simple Arrhenius kinetics predict a material decomposition rate of approximately 25 times greater at 120º C than at 75º C. Any material under test that exhibits gas evolution exceeding 4 cc/gm (approximately 0.8 % decomposition) is considered suspect and additional testing and/or evaluation is then performed to determine if the material is thermally unstable.

In addition to the CRT being significantly more severe and quantitative, there are significant other advantages for using the CRT. These include: (1) the increased safety afforded to operating personnel and equipment by using a fraction of the test material, (2) the cost savings associated with reduced sample heating time and the use of less sample material, and (3) the reduced amount of post-test waste produced.

Chemical Reactivity Test for Thermal Stability

1.0 Introduction

The Lawrence Livermore National Laboratory (LLNL) chemical reactivity test (CRT) is a thermal stability test which measures the amount of several gases evolved from an explosive

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sample after it has been exposed to a thermal environment for a period of time. The CRT is used as an alternative test to the Thermal Stability Test at 750 C. The explosive sample may also be mixed with another material to determine mutual compatibility. A measure of the reactivity is obtained when comparing the types and volumes of gases liberated from the mixture with the types and volumes of gases evolved by the individual components of the mixture.

Typically a 0.250 gm sample, under a helium blanket, is immersed in a 120º C bath for 22 hours. A minimum of two runs per sample are made on each material under test. Temperatures and/or times may be changed as required by the characteristics of the particular sample. Helium is used to sweep off any gaseous products of thermal decomposition through a gas chromatograph which has been programmed to analyze for N_2, O_2, Ar, CO, NO, CO_2, and N_2O. The results are given in terms of the sum (excluding Ar) of these volumes expressed as cc/gm.

The CRT is only run on a 0.250 gm sample rather than the ~50-100 gm sample specified by the Thermal Stability Test at 75º C, however, it is a much more severe test since it is run at 120º C rather than 75º C. Simple Arrhenius kinetics predict a material decomposition rate of approximately 25 times greater at 1200 C than at 75º C PBX-9404 is used as the reference material in this test. It evolves ~1.5 to 2.0 cc of gas per gram of explosive. Any material under test that exhibits gas evolution twice as great as PBX-9404 (4 cc/gm, approximately 0.8% decomposition) is considered suspect and additional tests and/or evaluation may be required to determine if the material is thermally unstable.

The CRT is normally run on an explosive composition as a powder unless it is a paste or a cast/cure PBX. Consolidated materials (pressed pellets) are generally not attempted. However, parallel tests on powders versus consolidated pellets on six explosive materials (see Section 5.0) showed that, except for PETN, there was not a significant difference between powders and consolidated pellets. In the case of PETN, the powder gave about twice the off-gas as pellets, but still less than PBX-9404. Therefore for most materials, either technique will give results applicable to both conditions. The CRT is not generally recommended for materials with high vapor pressures.

2.0 Apparatus and Materials

2.1 Apparatus

(1) A Hewlett Packard Model 5890 Series II gas chromatograph with a Model 3396 integrator is used to analyze the gas sample. A 20' by 1/8" OD Porapak Q 50-80 mesh molecular sieve is used in the chromatograph. Helium which has been passed through a liquid nitrogen cold trap is used as the carrier gas.

(2) A tank containing heated silicon brake fluid is used to heat the sample under test. Silicon brake fluid is used because it has low volatility and is thermally

stable. A temperature control unit which heats and circulates the fluid is attached to the tank. Temperature of the bath is maintained up to 120º C by the control unit to within ±1º C of the set point.

(3) Sample holder vessels called "loops" (see Figure 1), which are comprised of the following stainless steel components: a

sample holder with a valve, a diffusion plug (used as a weight),

a diffusion upper spacer, a crucible and a lower spacer. The internal volume of the loop is approximately 17 ml.

(4) An analytical balance capable of determining sample weight to ±0 .001 gm.

(5) A vacuum pump and vacuum system with pressure indicator. This system should be capable of evacuation down to approximately 10 millitorr.

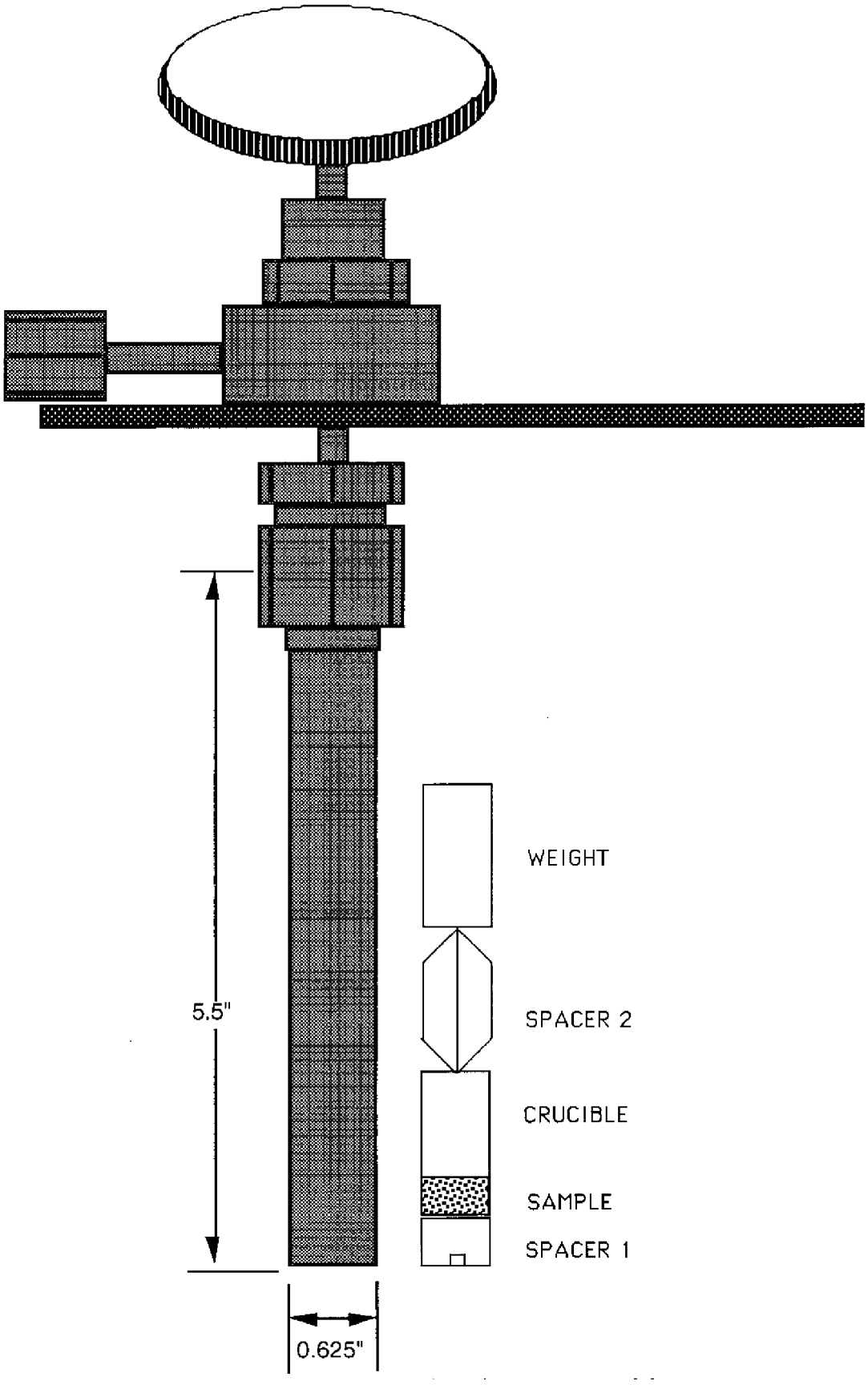
2.2 Materials

(1) A pressurized gas bottle containing small percentages of N_2, NO, N_2O, and CO_2 to be used as a calibration gas.

(2) A pressurized gas bottle containing ultra pure (99.999%) helium.

(3) Standard explosives as required. PBX-9404 is used as the reference material. An amount of a specific lot of PBX-9404 is set aside for future use as a standard.

Figure 1. CRT sample holder "loop" assembly. All loop components are made from stainless steel.



3.0 Procedure

3.1 Sample Preparation

(1) Prepare 2 crucibles with 0.250 gm +~0.001 gm of explosive sample. If chemical reactivity/compatibility tests are to be performed, thoroughly mix 0.250 gm of the explosive material with 0.250 gm of the material being tested (also preparing duplicate samples).

(2) After the 0.250 gm sample is carefully weighed on an analytical balance (0.500 gm mixture for reactivity/compatibility tests), it is then placed into the loop assembly.

3.2 Sample Loop Preparation and Heating

(1) The loop is then attached to a vacuum rack and evacuated until all outgassing quits. Flush with helium if necessary.

(2) Backfill the sample loop with 1 atmosphere of helium.

(3) Remove the sample loop from the vacuum system and place the sample loop into the silicon bath. Note the time the sample loop is placed into the bath.

(4) At the end of the 22 hour heating cycle, the sample loop is removed from the bath and allowed to come to ambient temperature before running the gas analysis.

3.3 Sample Gas Analysis

(1) The gas chromatograph is routinely calibrated with a calibration gas containing a known small percentage of each of the gasses being analyzed. In addition, PBX-9404 should be routinely run since it is used as the standard.

(2) Prepare the gas chromatograph for sample gas analysis. The equipment is turned on and allowed to warm up.

(3) Information for each sample loop is entered through the chromatograph integrator prior to sample analysis. This should include as much about the material as possible (e.g., material name and any other numbers or letters that will identify it, sample amount, temperature at which it was heated, the present job number, etc.).

(4) Obtain LN and fill the cold trap to cool the helium purge supply.

(5) Check helium gas supply regulator and adjust to 60 psi.

(6) Turn on the CO_2 supply to cool the gas chromatograph. The gas chromatograph takes several minutes to reach its operating temperature of -40° C and takes about 3 minutes to stabilize.

(7) Connect the sample loop to the vacuum manifold and evacuate the air at the connection.

(8) When the gas chromatograph is stabilized, the sample loop valve is opened and the gas chromatograph is started.

(9) After a couple of minutes into the run, the sample loop can be removed and replaced with a new sample. The air must again be evacuated at the connection.

(10) Once the samples have been run, all sample loop hardware must be cleaned with isopropyl alcohol after each run. In addition, the part of the loop which contains the explosive sample is heated overnight in an oven to drive off any volatile materials.

4.0 Criteria and Method of Assessing Results

4.1 Thermal Stability

A test result is considered positive (i.e., thermally unstable) if ignition or an explosion occurs. If the CRT gas volumes produced are in excess of 4 cc/gm (approximately 0.8% decomposition), additional tests (e.g., decreasing CRT temperature to 100 or 800 C and increasing the time to 48 hours) and/or evaluation may be required to determine if the material is thermally unstable. If the CRT gas volumes produced are less than 4 cc/gm, the material is considered thermally stable. For reference purposes, 1 cc of evolved gas/gm of explosive represents about 0.2% decomposition.[6]

4.2 Chemical Reactivity/Compatibility for a Mixture

(1) If the CRT gas volume of the mixture is equal to or less than the sum of the individual components, there is no evidence of chemical reactivity and the mixture is considered chemically compatible and unreactive.

(2) If the CRT gas volume of the mixture is significantly greater than the sum of the individual components, there is evidence of chemical reactivity and the mixture should be considered incompatible on the basis of this test. Other testing such as differential scanning calorimetry (DSC) and /or analysis is required. Generally, total gas volumes of the mixture that are between 1.0 and 1.5 cc/gm are moderately reactive and the materials are considered incompatible.

Note: These numbers are only to be used as general guidelines and are not to

be used as defining criteria. All data should be reviewed by a qualified person, who has a good understanding of what the presence of the various decomposition products (including at various temperatures) really means. The sum of the gas products of the individual components should be carefully compared to the total gas products of the mixture to determine where the differences occur and if they are significant.

5.0 Examples of Results

Typical Individual Gas Evolution Results (cc/0.250 gm at 120° C for 22 hours)[7]

Explosive Material	N_2	O_2	CO	NO	CO_2	N_2O	Total
PETN (powder)	0.046	0	0.038	0.080	0.131	0.014	0.309
PETN (pellet)	0.013	0	0.011	0.028	0.069	0.005	0.126
Comp B (powder)	0.011	0	0	0.024	0.039	0.018	0.092
Comp B (pellet)	0.014	0	0	0.021	0.018	0.020	0.073
LX-14 (powder)	0	0	0	0	0.053	0.006	0.059
LX-14 (pellet)	0	0	0	0.004	0.016	0.006	0.026
LX-17 (powder)	0	0	0	0	0.023	0	0.023
LX-17 (pellet)	0	0	0	0	0.042	0	0.042
PBX-9404 (powder)	0.020	0	0.039	0.244	0.137	0.023	0.463
PBX-9404 (pellet)	0.056	0	0.049	0.171	0.198	0.039	0.513

Typical Individual Gas Evolution Results
(cc/0.250 gm at 120° C for 22 hours)[7]

Composition of Explosive Material Compounds

PETN	Pentaerythrol tetranitrate
Comp B	63% RDX (trinitro-triazocyclohexane) 36% TNT (trinitrotoluene) 1% Wax
LX-14	95.5% HMX (tetranitro-tetrazo-cyclooctane) 4.5% Estane 5702-F1 (hydrocarbon polymer binder)
LX-17	92.5% TATB (triaminotrinitrobenzene) 7.5% Kel-F 800 (fluoropolymer binder)
PBX-9404	94% HMX 2.9% Nitrocellulose 3.0% Tris-β-chloroethyl-phosphate plasticizer (CEF) 0.1% Diphenylamine

Composition of Explosive Material Compounds

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